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The molecular nature of an excess proton in water remains one of oldest unsolved problems at the heart of aqueous chemistry. In a close collaboration, two experimental groups [Johnson (Yale) and Duncan (Georgia)] have isolated protonated water clusters and used vibrational spectroscopy to characterize how networks of water molecules act cooperatively to accommodate the extra proton.

The spectral signatures of the free or dangling OH groups display a remarkable collapse upon addition of the 21st water molecule (yellow spectrum, upper right figure), a size that appears unusually abundant or “magic” in the ion source. Because 20 water molecules are known to form clathrate structures, these spectra were compared with the expected behavior of low energy (0 K) water nanocages, calculated by Jordan’s group at Pittsburgh. Although the spectral collapse can be explained in the context of the calculated minimum energy structures, a surprising result is that the bands associated with the H_3O^+ “Eigen” cation are *missing* in the observed spectra. This raises the specter that under the warmer (150-200 K) experimental conditions, the proton is actually delocalized over several oxygen atoms, perhaps involving so-called Zundel ions, H_5O_2^+ .

